NASA

National Aeronautics and
Space Administration

Washington, D.C.
20546

Lewis

Reply to Attn of: GP-4

AUG 3 1981

TO: NST-44/Scientific and Technical Information Division
Attn: Shirley Peigare

FROM: GP-4/Office of Assistant General Counsel
for Patent Matters/Nancy L. Fonseca

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP-4 and Code NST-44, the attached NASA-owned U.S. Patewnt is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. : 4,270,984

Government or
Corporate Employee : Giner, Inc.
Waltham, MA 02154

Supplementary Corporate
Source (if applicable) :

NASA Patent Case No. : LEW-13,148-2

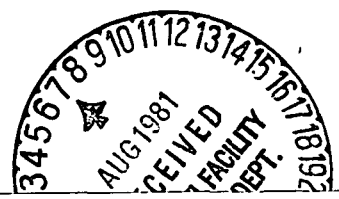
NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

YES [X] NO [ ]

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of column No. 1 of the Specification, following the words "...with respect to an invention of..."

Nancy L. Fonseca

Enclosure



(NASA-Case-LEW-13148-2) CATALYST SURFACES FOR THE CHROMOUS/CHROMIC REDOX COUPLE Patent (NASA) 8 p CSCL 10C

N81-29524

Unclas
00/44 31200

LEW-13,148-2

United States Patent [19]

Giner et al.

[11] **4,270,984**

[45] **Jun. 2, 1981**

[54] **CATALYST SURFACES FOR THE CHROMOUS/CHROMIC REDOX COUPLE**

[76] Inventors: **Robert A. Frosch**, Administrator of the National Aeronautics and Space Administration, with respect to an invention of **José D. Giner; Kathleen J. Cahill**, both of Waltham, Mass.

[21] Appl. No.: **61,555**

[22] Filed: **Jul. 27, 1979**

Related U.S. Application Data

[62] Division of Ser. No. 964,754, Nov. 29, 1978, Pat. No. 4,192,910.

[51] **Int. Cl.**[3] **H01M 10/44**

[52] **U.S. Cl.** **204/2.1**

[58] **Field of Search** ..... 204/2.1, 46 R, 46 G, 204/50 R, 53

[56] **References Cited**

U.S. PATENT DOCUMENTS

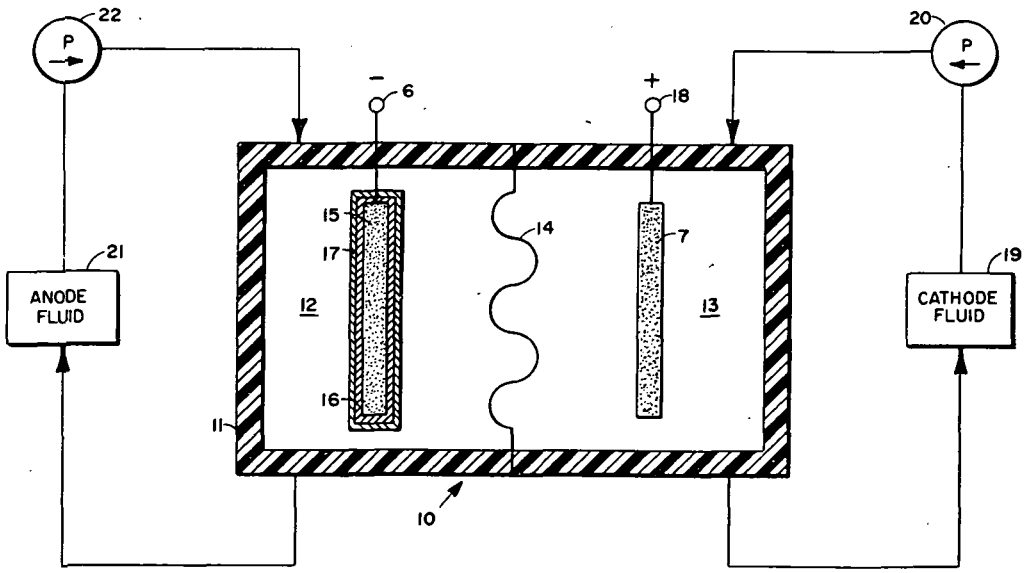
3,178,315	4/1965	Worsham	429/46
3,279,949	10/1966	Schaefer	429/46
3,540,934	11/1970	Boeke	429/101
3,996,064	12/1976	Thaller	429/34
4,159,366	6/1979	Thaller	429/15

Primary Examiner—T. M. Tufariello
Attorney, Agent, or Firm—N. T. Musial; J. R. Manning; J. A. Mackin

[57] **ABSTRACT**

There is disclosed an electricity producing cell of the reduction-oxidation (REDOX) type divided into two compartments by a membrane, each compartment containing a solid inert electrode. A ferrous/ferric couple in a chloride solution serves as a cathode fluid which is circulated through one of the compartments to produce a positive electric potential disposed therein. A chromic/chromous couple in a chloride solution serves as an anode fluid which is circulated through the second compartment to produce a negative potential on an electrode disposed therein. The electrode is an electrically conductive, inert material plated with copper, silver or gold. A thin layer of lead plates onto the copper, silver or gold layer when the cell is being charged, the lead ions being available from lead chloride which has been added to the anode fluid. If the REDOX cell is then discharged, the current flows between the electrodes causing the lead to deplate from the negative electrode and the metal coating on the electrode will act as a catalyst to cause increased current density.

18 Claims, 4 Drawing Figures



LEW-13,148-2

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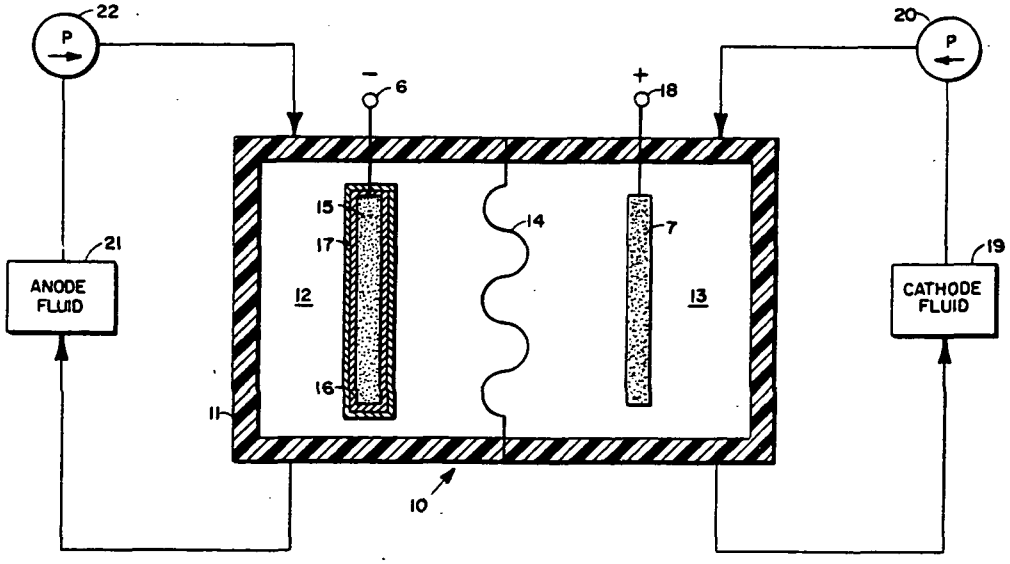

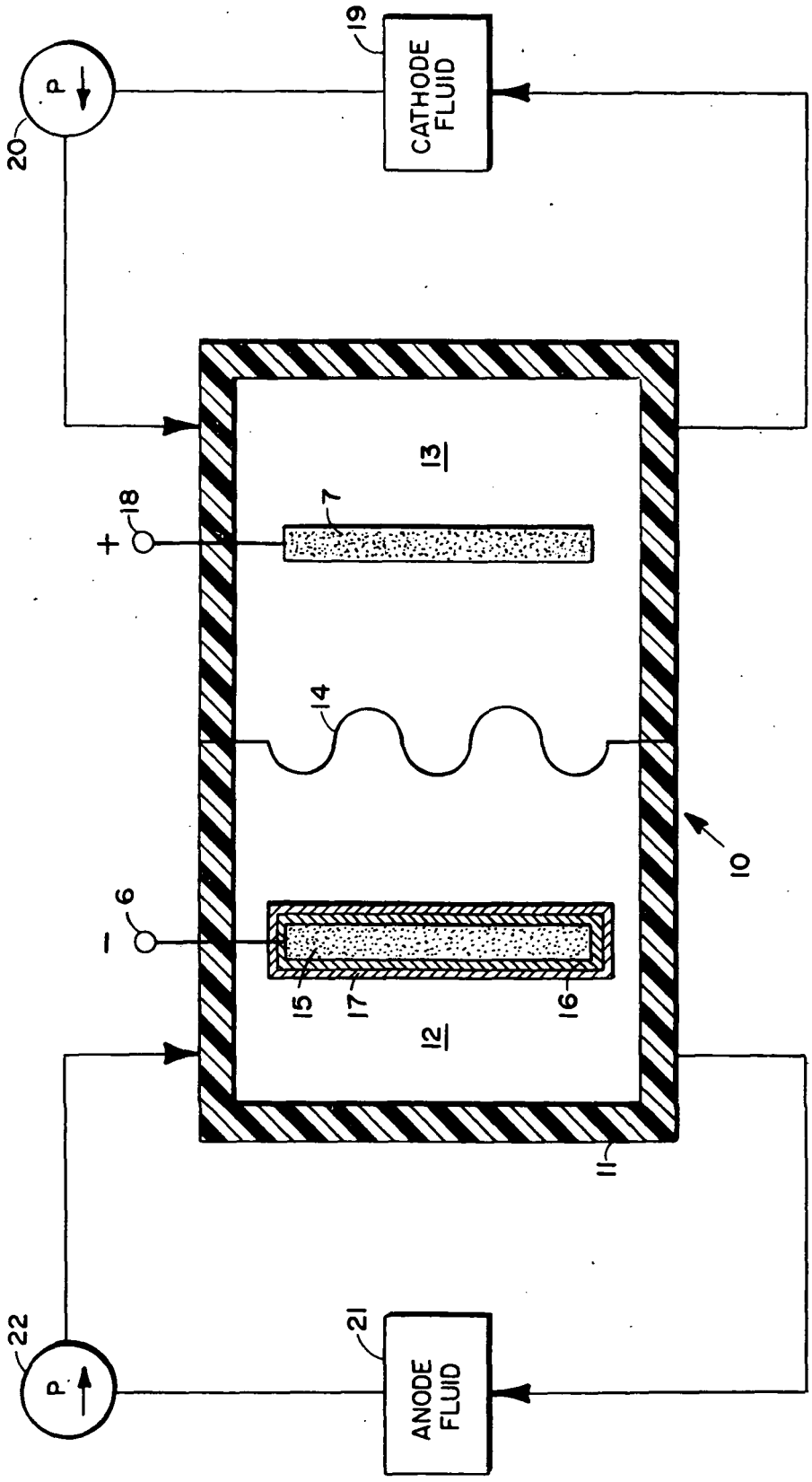
19
CATHODE FLUID
P
20
13
18
+
7
14
10
6
-
15
17
16
12
11
22
P
21
ANODE FLUID

FIG. 1

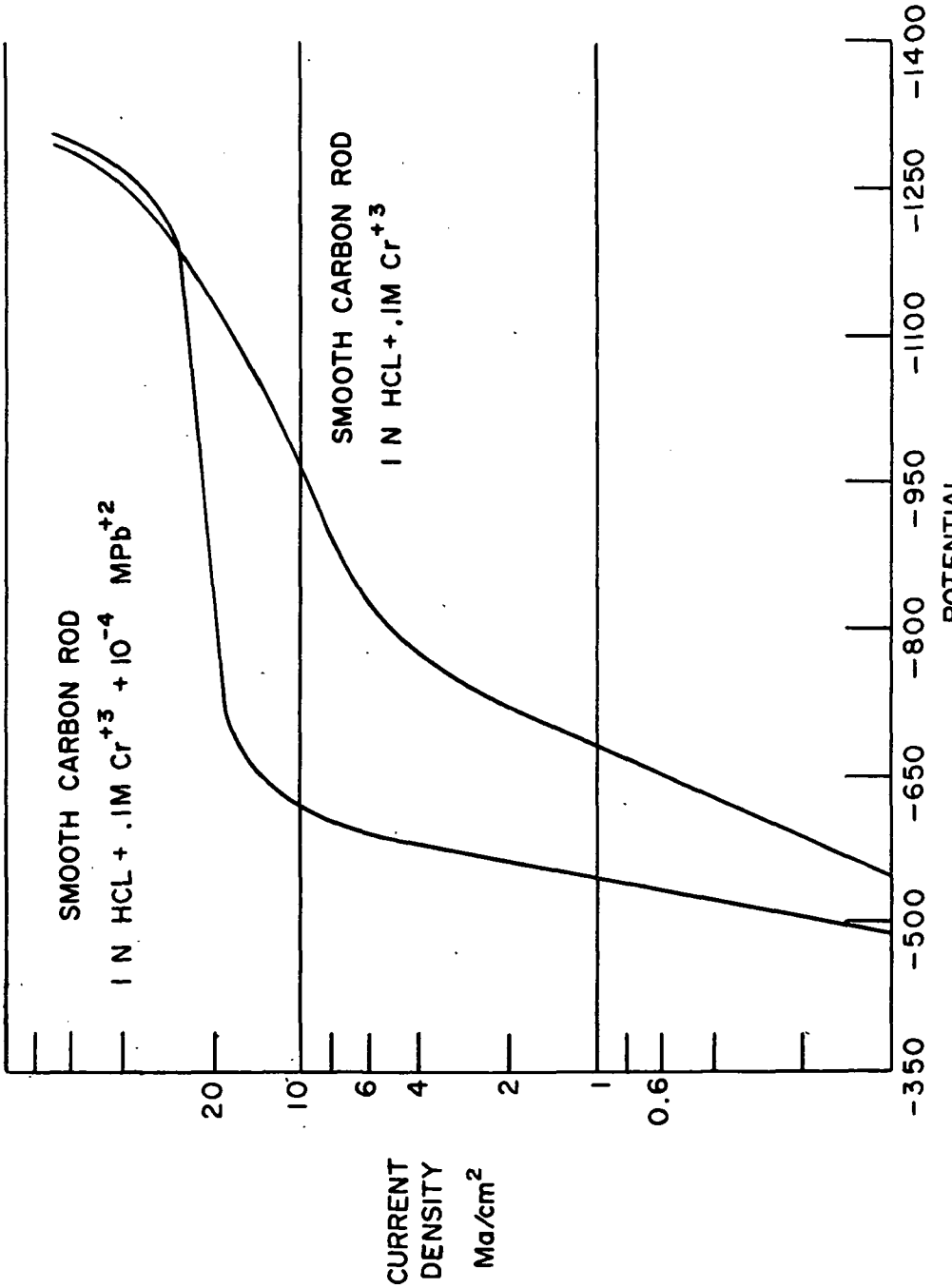
SMOOTH CARBON ROD
1 N HCL + .1M Cr^{+3} + 10^{-4} MPb^{+2}
SMOOTH CARBON ROD
1 N HCL + .1M Cr^{+3}
CURRENT DENSITY Ma/cm²
20
10
6
4
2
1
0.6
-350
-500
-650
-800
-950
-1100
-1250
-1400
POTENTIAL MV VS. SCE

FIG. 2

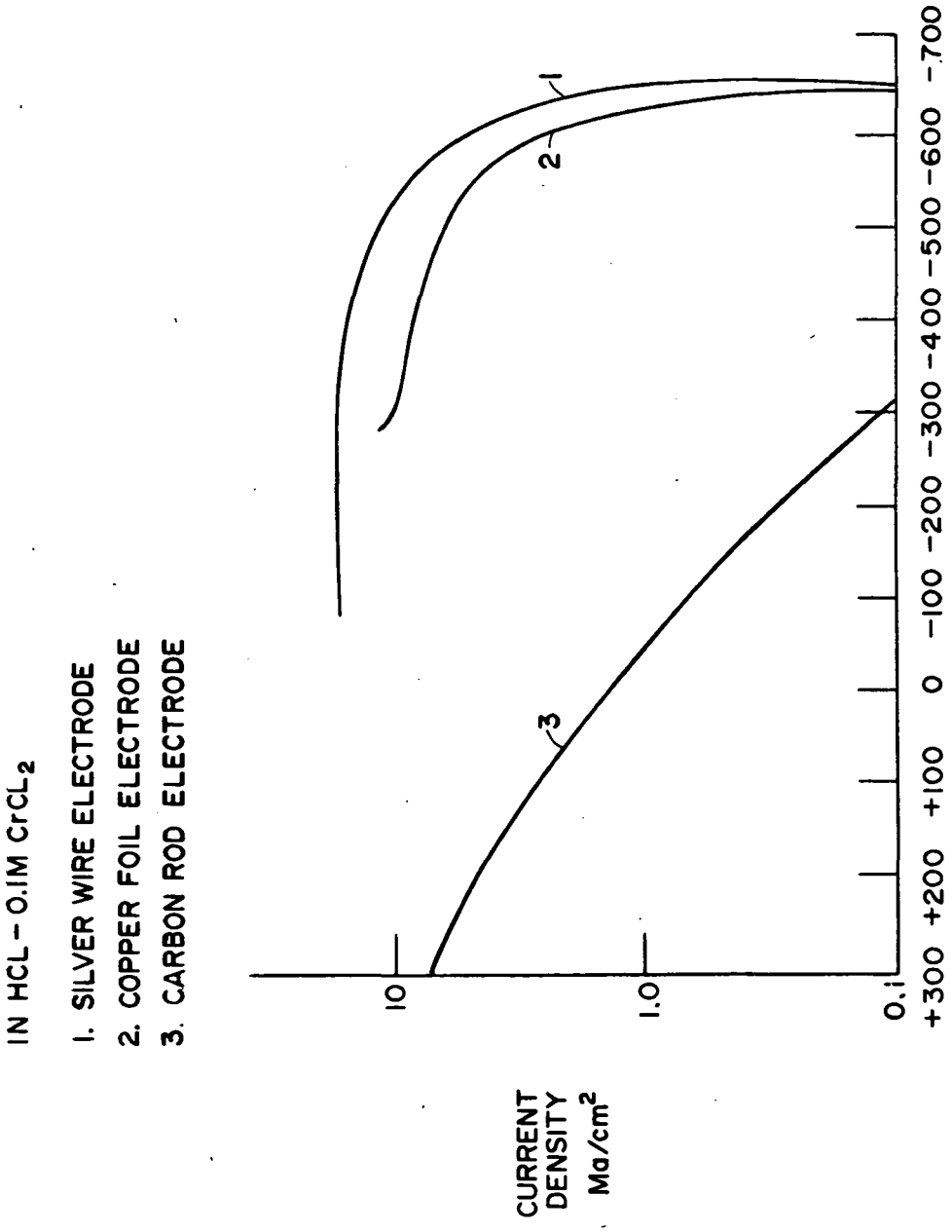
IN HCL – 0.1M $CrCl_2$
1. SILVER WIRE ELECTRODE
2. COPPER FOIL ELECTRODE
3. CARBON ROD ELECTRODE
CURRENT DENSITY Ma/cm²
10
1.0
0.1
+300 +200 +100 0 -100 -200 -300 -400 -500 -600 -700
POTENTIAL MV VS. SCE
1
2
3

FIG. 3

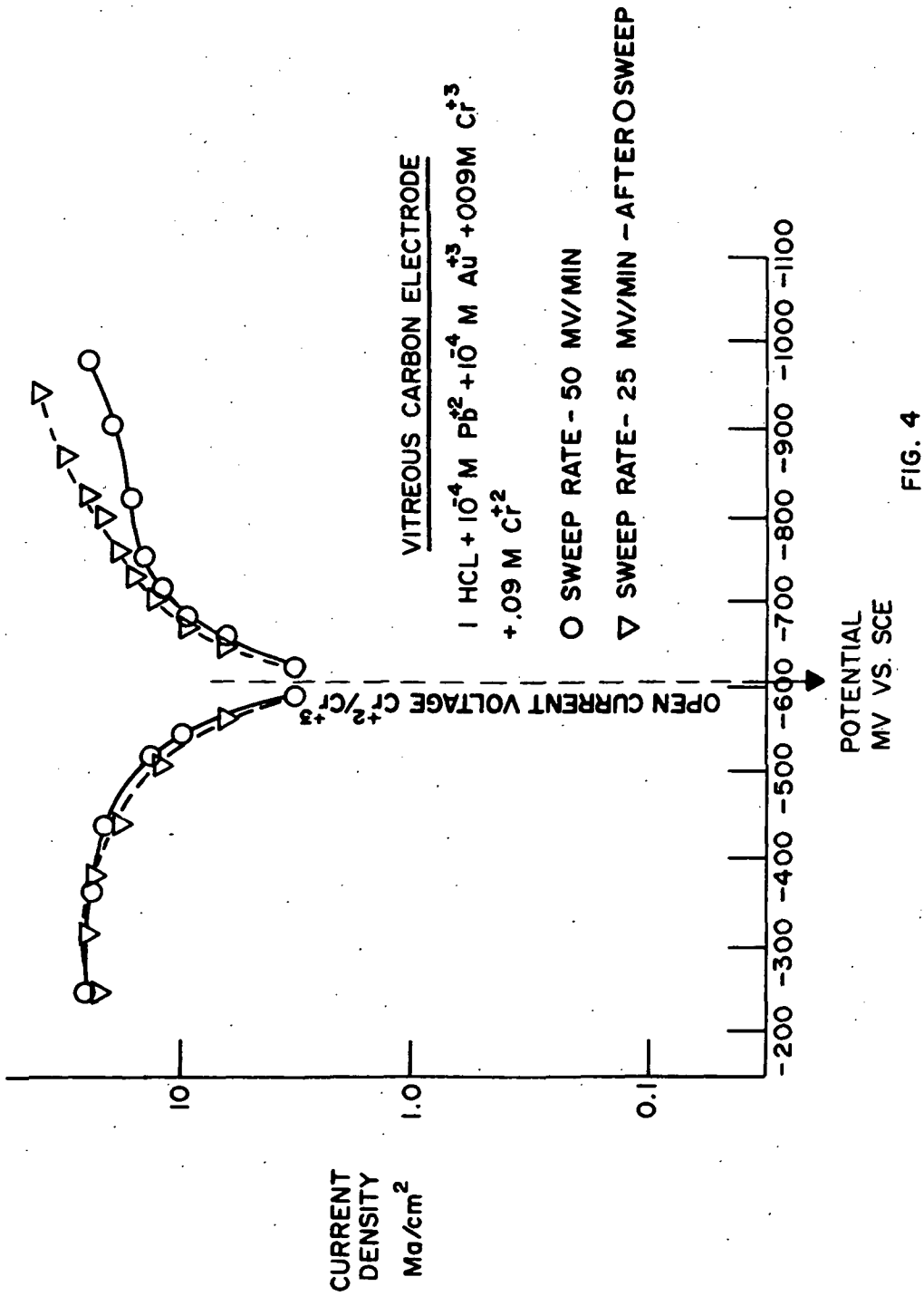
VITREOUS CARBON ELECTRODE
1 HCL + 10^{-4} M Pb^{+2} + 10^{-4} M Au^{+3} + .009M Cr^{+3}
+ .09 M Cr^{+2}
O SWEEP RATE - 50 MV/MIN
∇ SWEEP RATE - 25 MV/MIN - AFTER O SWEEP
OPEN CURRENT VOLTAGE Cr^{+2}/Cr^{+3}
CURRENT DENSITY Ma/cm²
10
1.0
0.1
-200 -300 -400 -500 -600 -700 -800 -900 -1000 -1100
POTENTIAL MV VS. SCE

FIG. 4

CATALYST SURFACES FOR THE CHROMOUS/CHROMIC REDOX COUPLE

This is a division, of application Ser. No. 964,754, filed Nov. 29, 1978 now U.S. Pat. No. 4,192,910.

BACKGROUND OF THE INVENTION

Because of the energy crisis beginning in the mid-1970's and due to economic factors within the electric utility industry, there is a need for storing bulk quantities of electrical power which might be produced intermittently or randomly by devices such as wind-driven generators, solar cells or the like. A number of methods have been considered including the storage of compressed air in large reservoirs, flywheels, capacitive storage, inductive storage and a number of electrochemical schemes. Electrochemical storage batteries are generally expensive, heavy and subject to deterioration when subjected to repeated charge and discharge actions.

Up until now, only pumped water storage wherein water from a water storage pond at one level is directed to a water storage pond at a lower level through a hydro-electric plant having a water pumping capability has proven to be a viable method. Unfortunately, such facilities are limited to areas where the terrain is suitable for providing water sources at different elevations.

Electrically rechargeable REDOX flow cell systems are well known and have a very high overall energy efficiency as compared to other systems. Furthermore, REDOX type cells can be discharged more completely than secondary battery systems. Additionally, REDOX cells are inexpensive as compared to secondary batteries and do not deteriorate as significantly when repeatedly discharged in recharge.

DESCRIPTION OF THE PRIOR ART

As indicated previously, REDOX electrical cells are well-known. One of the best known REDOX cells uses an anode fluid having a chromic/chromous couple and a cathode fluid having ferrous/ferric couple. In the prior art, electric potential from such a REDOX cell was obtained by terminals connected to respective inert electrodes, one being disposed in the anode fluid and the other being disposed in the cathode fluid. Carbon and graphite products which are inert to the anode and cathode fluids were used as electrodes in some cases.

OBJECTIVES AND SUMMARY OF THE INVENTION

It is an object of the invention to provide a REDOX cell which will deliver much greater current for any given electrode surface area than prior art devices.

It is another object of the invention to provide a REDOX type cell which will deliver an increasingly greater percentage of current when compared to prior art REDOX cells as the cell approaches a discharged condition.

Still another object of the invention is to provide a method of making a REDOX cell wherein certain desirable ions are provided in one of the fluids to produce a coating on its associated electrode as the REDOX cell is charged.

Yet another object of the invention is to provide a REDOX cell having a catalytic coating on one of the electrodes to enhance the activity of the desired ions in the one fluid.

In summary, there is provided a REDOX cell which may or may not have a catalytic coating on one electrode but including certain desired ions in the fluid which contacts the electrode to coat it with the ions as charging takes place.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of the REDOX cell embodying the invention showing the anode and cathode fluid supply systems schematically.

FIG. 2 is a graph illustrating the increased current density in a REDOX cell embodying the invention.

FIG. 3 is a graph illustrating current density versus potential for different electrode materials.

FIG. 4 illustrates current density versus potential for a carbon electrode with a catalytic coating and utilizing desired ions in the fluid to plate out on the coated electrode.

DESCRIPTION OF A PREFERRED EMBODIMENT

Referring now to FIG. 1, there is shown a REDOX cell **10** comprising container **11**, divided into compartments **12** and **13** by an ion conductive membrane **14**. The graphite electrode **15** is disposed in the chamber **12** and connected to an output terminal **6** while a graphite electrode **7** is disposed in compartment **13** and connected to an output terminal **18**.

In order to produce a voltage or potential difference between terminals **6** and **18**, a cathode fluid is passed through chamber **13** while an anode fluid is passed through chamber **12**. As shown, cathode fluid from a cathode fluid source **19** is circulated by a pump **20** through compartment **13**. Similarly, anode fluid from an anode fluid source **21** is circulated by a pump **22** through the compartment **13**.

The REDOX cell **10** utilizes an iron/chromium system wherein the cathode fluid contains ferrous/ferric couple while the anode fluid contains a chromic/chromous couple. The anode fluid preferably contains water and HCl (aqueous solution of HCl) having dissolved therein a chromium chloride salt. The cathode fluid likewise is water and HCl but has dissolved therein an iron chloride salt. These fluids provide the desired couples in each of the chambers **11** and **12**. A more complete discussion of the couple, the fluid electrode requirements and membrane considerations is given in U.S. Pat. No. 3,996,064 which is incorporated herein by reference. In accordance with the present invention, it has been found that a coating of lead on the inert electrode **15** substantially increases the current density of the electrode, and consequently, the current available at terminals **6** and **18**. The lead may be coated onto the electrode **15** before it is disposed in chamber **12** to be contacted by the circulating anode with fluid. It can also be obtained by dissolving lead chloride in the anode fluid before charging the REDOX cell.

When current is supplied to the REDOX cell **10** at terminals **6** and **18** to bring it up to a charged condition, a lead coating will deposit on the anode electrode **15**. Conversely, as the REDOX cell is discharged by current drawn from the terminals **6** and **18**, the lead deplates from the electrode and is redissolved into the anode fluid.

When the REDOX cell is being charged, chromium reduction occurs very rapidly on the lead surface which is desirable for high current density. At the same time, the rate of hydrogen evolution is advantageously mini-

an electrically conductive inert electrode disposed in the anode fluid.

2. The method of claim 1 wherein the lead ions produced in said anode fluid by the lead chloride are in the amount of 10^{-4} to 10^{-5} M/liter of anode fluid.

3. The method of claim 1 wherein an electrode to be inserted in the anode fluid is first coated with a metal selected from the group consisting of lead, silver, gold and copper.

4. The method of claim 3 wherein said metal coating is from about 2 to about 5 monolayers thick.

5. A method of making a REDOX cell of the type having an ion permeable membrane separating anode and cathode fluids comprises of water, HCl and chromium and iron chloride salts, respectively, and including the step of coating lead onto an electrically conductive inert electrode before disposing the electrode in the anode fluid.

6. The method of claim 5 wherein the lead coating is from about 2 to about 5 monolayers thick.

7. The method of claim 5 and including the additional step of coating the inert electrode with a coating selected from the group of metals consisting of lead, silver, gold and copper before applying the lead coating.

8. The method of claim 7 wherein the metal coating is from about 2 to about 5 monolayers thick.

9. The method of claim 1 wherein a porous inert electrode to be disposed in the anode chamber is first saturated with a solution of a salt selected from the group consisting of gold chloride, silver chloride and copper chloride and then heat treated.

10. A method of making a REDOX cell of the type having an ion permeable membrane separating anode and cathode fluids comprised of water, HCl and chromium and iron chloride salts, respectively, and including the additional steps of adding cadmium chloride to the anode fluid and then charging the cell to plate cadmium onto an electrically conductive inert electrode disposed in the anode fluid.

11. The method of claim 10 wherein the cadmium ions produced in said anode fluid by the cadmium chloride are in the amount of 10^{-4} to 10^{-5} M/liter of anode fluid.

12. The method of claim 10 wherein an electrode to be inserted in the anode fluid is first coated with a metal selected from the group consisting of silver, gold and copper.

13. The method of claim 12 wherein said metal coating is from about

14. A method of making a REDOX cell of the type having an ion permeable membrane separating anode and cathode fluids comprised of water, HCl and chromium and iron chloride salts, respectively, and including the step of coating cadmium onto an electrically conductive inert electrode before disposing the electrode in the anode fluid.

15. The method of claim 12 wherein the cadmium coating is from about 2 to about 5 monolayers thick.

16. The method of claim 14 and including the additional step of coating the inert electrode with a coating selected from the group of metals consisting of silver, gold and copper before applying the cadmium coating.

17. The method of claim 16 wherein the metal coating is from about 2 to about 5 monolayers thick.

18. A method of increasing the current output of a REDOX cell of the type having an ion permeable membrane separating anode and cathode chambers, each chamber containing an electrically conductive electrode, the anode chamber containing a fluid comprised of aqueous HCl having chromium chloride dissolved therein, the cathode chamber containing a fluid comprised of aqueous HCl having iron chloride dissolved therein, the method comprising the steps of: adding to said anode fluid more than one salt selected from the group consisting of lead chloride and cadmium chloride and then charging said cell to plate cadmium and lead onto the electrode in the anode chamber.

* * * * *